Janet Napolitano, Governor
Stephen A. Owens, Director

DETERMINATION OF DE MINIMIS LEVELS

Prepared for
Arizona Department of Environmental Quality
1110 West Washington Street
Phoenix, Arizona 85007

Prepared by
Weston Solutions
950 West Elliot Road #110
Tempe, Arizona 85284

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List of Acronyms

AAC	ambient air concentrations
ADEQ	Arizona Department of Environmental Quality
A.R.S.	Arizona Revised Statutes
CAAA	Clean Air Act Amendments
EPA	Environmental Protection Agency
g/s	grams per second
HAP	Hazardous Air Pollutant
HAPRACT	Hazardous Air Pollutant Reasonable Available Control Technology
hr/yr	hour per year
K	Kelvin
lb/yr	pound per year
MACT	Maximum Achievable Control Technology
m	meter
mg/m^3	milligrams per cubic meter
m/s	meter per second
RMA	Risk Management Analysis
tpy	ton per year

1.0 INTRODUCTION

1.1 Objective

The objective of this task is to determine the levels of emission increases of hazardous air pollutants (HAPs) at existing sources that will trigger applicability of the state HAPs program. These levels are referred to in the state air quality statute as "de minimis." Physical or operational changes resulting in greater than de minimis increases in HAP emissions are known as "modifications." Sources that undergo modifications will potentially be subject to the requirement to install hazardous air pollutant reasonably available control technology or maximum achievable control technology. This task seeks to establish de minimis levels that reflect the maximum amount of a specified pollutant which could be emitted as the result of a modification without producing adverse impacts on human health.

1.2 Background

In 1992, legislation was adopted to control sources of HAPs that would not be addressed under § 112 of the federal Clean Air Act Amendments of 1990 (CAAA). Arizona Revised Statutes (A.R.S.) §§ 49-426.04, 49-426.05 and 49-426.06, required Arizona Department of Environmental Quality (ADEQ) to adopt rules by November 15, 1993, for the case-by-case imposition of control technology on new and modified sources of HAPs.

A.R.S. § 49-426.06 provides that the list of HAPs subject to the program includes all federal HAPs listed under section 112(b) of the CAAA. It also authorizes the ADEQ to adopt rules designating additional state HAPs. A.R.S. § 49-426.06 provides that new and modified sources of HAPs with the potential to emit 10 tons per year (tpy) of a single HAP or 25 tpy of a combination of HAPs are subject to Maximum Achievable Control Technology (MACT). New and modified smaller sources are subject to less stringent standards, called Hazardous Air Pollutant Reasonably Available Control Technology (HAPRACT), but only if they meet two qualifications: (1) they emit more than 1 tpy of a single HAP or 2.5 tpy of a combination of HAPs; and (2) they belong to a category of sources designated by rule by ADEQ. A.R.S. § 49-426.05 provides that ADEQ may designate a source category as being subject to the program at the lower thresholds, if "emissions from sources in the category individually or in the aggregate result in adverse effects to human health or adverse environmental effects."

A modification is defined in A.R.S. § 49-401.01(24) as "a physical change in or change in the method of operation of a source which increases the actual emissions of any regulated air pollutant emitted by such source by more than a relevant de minimis amount or which results in the emission of any regulated air pollutant not previously emitted by more than such de minimis amount." In anticipation of EPA adopting de minimis amounts for federal HAPs under section 112(g) of the CAAA, A.R.S. § 49-426.06(B) provides that ADEQ "shall by rule establish appropriate de minimis amounts for [HAPs] that are not federally listed [HAPs]." Because EPA has failed to adopt de minimis amounts for federal HAPs when it adopted rules under section 112(g), ADEQ must adopt de minimis amounts for federal HAPs, as well as any state HAPs that may be listed.

Sources subject to the state HAPs program may demonstrate that the imposition of MACT or HAPRACT is not necessary to avoid adverse effects to human health or the environment by preparing a Risk Management Analysis (RMA) considering estimated actual exposure, available epidemiological or other health studies, background concentrations, uncertainties in risk or health assessment, and other factors. In cases where the Director issues a general permit establishing MACT or HAPRACT, sources covered by the permit could avoid the requirements by submitting an RMA.

In 1995, the legislature enacted HB 2198, which removed the deadline for adopting the State HAPs program rules. In 1996, the legislature enacted HB 2547, which made technical corrections to the provisions governing implementation of the HAPs program and specified that in determining potential to emit, "the director shall exclude particulate matter emissions that consist of natural crustal material and are produced by natural forces…or by anthropogenic sources such as agricultural operations, excavation, blasting, drilling, handling, storage, earth moving, crushing, grinding or traffic over paved and unpaved roads, or other similar activities."

1.3 Development of De Minimis Levels

ADEQ determined that de minimis levels should reflect the maximum amount of a specified pollutant that could be emitted as the result of a modification without producing adverse impacts on human health.

The methodology used to calculate the de minimis levels is as follows:

- Based on information developed by ADEQ, seventy-three (73) HAPs were identified as being emitted from facilities in Arizona in quantities greater than the 1 or 2.5 tpy threshold levels.
- For each of these HAPs, chronic and acute health-based Ambient Air Concentrations (AACs) were developed. These are presented in separate reports that were distributed prior to, and discussed at, the July 19, 2005, stakeholder meeting (see WESTON, 2005a and WESTON, 2005b).
- A dispersion model was used to determine the concentration-to-emission-rate ratio for a hypothetical facility with worst-case emission dispersion characteristics (see discussion in Section 2.0).
- The health-based AAC for each pollutant was then divided by the concentration-to-emission-rate ratio to calculate de minimis levels (see results in Section 3.0).

This report discusses the development of the criteria for determining the de minimis levels and the resulting calculated de minimis levels.

2.0 MODELING APPROACH

The approach follows ADEQ and EPA modeling guidance (ADEQ, 2004 and EPA, 1996). The SCREEN3 model (version 96043, EPA, 1995) was used to determine de minimis amounts for the 73 HAP pollutants where the health-based criteria have been established (WESTON, 2005a and WESTON, 2005b). The SCREEN3 model was run with a 1 gram per second (g/s) emission rate. From this, a ratio representing the 1-hour maximum concentration resulting from a 1 g/s emission rate (concentration-to-emission-rate ratio) was derived. The measurement units for the ratio are milligrams per cubic meter divided by grams per second or $(mg/m^3)/(g/s)$.

In the SCREEN3 model, the emission rate is directly proportional to the modeled concentration. Therefore, the emission rate that would produce results equal to the health-based ambient air concentration (AAC) for each pollutant can be derived by dividing the AAC by the concentration-to-emission-rate ratio.

De minimis emission rates will be applied to many types of facilities with a wide variety of stack parameters and configurations. In order to assure that any emission increases that may adversely affect public health are evaluated, a hypothetical facility with worst-case emission dispersion characteristics was used to determine the concentration-to-emission-rate ratio. Specifically, the following stack parameters were used to simulate a reasonable worst-case scenario:

- Emission rate – 1 g/s
- Stack height – 5.64 meters (m)
- Stack exit velocity – 0.001 meter per second (m/s) (ADEQ, 2004)
- Stack exit temperature – 293 ^{o}Kelvin (K)
- Stack diameter – 1 m

The following model options were used:

- Flat terrain
- No flag pole receptors

- Rural dispersion curves
- Building dimensions – 3.66 m tall, 40 m long, and 40 m wide. These dimensions were determined to result in a worst-case ground level concentration for a 5.64 m stack.
- Receptors – automatically generated by the SCREEN3 model beginning at the stack base and extending to 10,000 m.
- Full meteorology – this meteorological dataset is inherent in the SCREEN3 models and represents worst-case conditions.

Once the concentration-to-emission-rate ratio is determined, de minimis amounts can be calculated by dividing the AAC for each pollutant and averaging period by the ratio and converting to the appropriate averaging-period. The calculation is performed using the following simple equation:

$$E_d = AAC / CER$$

where,

E_d = Calculated de minimis emission rate (g/s)

AAC = ambient air concentration either annual or hourly (mg/m^3)

CER = concentration - to - emission - rate ratio {(mg/m^3)/(g/s)}

To calculate a pound per hour (lb/hr) de minimis emission rate, E_d would be divided by 0.126{(g/s)/(lb/hr)}. To calculate annual de minimis emissions, the modeled concentration would be converted to an annual concentration by multiplying by 0.08 as recommended in ADEQ guidance (ADEQ, 2004), then E_d would be divided by 0.126 and multiplied by 8,760 hours per year.

Using the above stack parameters and assumptions, the generic hourly modeled concentration was determined to be 143.2 (mg/m^3)/(g/s). Each AAC has been divided by this ratio and then converted to the relevant averaging period to derive the appropriate de minimis amount.

The SCREEN3 model output is available on request.

The following example details calculations of de minimis rates for benzene. First, the short-term de minimis emission rate in grams per second is calculated:

Hourly benzene AAC – 1,276 mg/m^3

Modeled hourly generic concentration – 140.3 $(mg/m^3)/(g/s)$

E_d (g/s) = 1,276 (mg/m^3)/{140.3 $(mg/m^3)/(g/s)$} = 9.09 (g/s)

E_d (lb/hr) = 9.09 (g/s) / {0.126 (g/s)/(lb/hr)} = 72 lb/hr

For the annual benzene de minimis level, the calculations are as follows:

Annual AAC – 2.43E-04 mg/m^3

Modeled annual concentration – 140.3$(mg/m^3)/(g/s)$ x 0.08 = 11.2 $(mg/m^3)/(g/s)$

E_d (g/s) = 2.43 E-04 (mg/m^3)/{11.2 $(mg/m^3)/(g/s)$} = 2.17 E-05 (g/s)

E_d (lb/hr) = 2.17 E-05 (g/s) / {0.126 (g/s)/(lb/hr)} x 8,760 (hr/yr) = 1.5 lb/yr.

Where, as in this case, the annual de minimis emission rate is lower than the hourly rate, only an annual rate will be specified.

3.0 RESULTS

Table 3-1 shows the calculated de minimis values based on acute and chronic health-based ambient air criteria. If the facility-wide emission increase for any pollutant exceeds any of the values shown in Table 3-1, an RMA would need to be conducted to demonstrate that emissions of that specific pollutant will not cause adverse affects to human health or the environment. If this cannot be demonstrated, HAPRACT should be determined.

Table 3-1 Calculated De Minimis Levels

Chemical	Acute AAC (mg/m^3)	De Minimis (lb/hr)	Chronic AAC (mg/m^3)	De Minimis (lb/yr)
1,1,1-Trichloroethane (Methyl Chloroform)	2,075	117	2.30E+00	14,247
1,1,2,2-Tetrachloroethane	18	a	3.27E-05	0.20
1,3-Butadiene	7,514	a	6.32E-05	0.39
1,4-Dichlorobenzene	300	a	3.06E-04	1.9
2,2,4-Trimethylpentane	900	51	NA	-
2,4-Dinitrotoluene	5.0	a	2.13E-05	0.13
2-Chloroacetophenone	NA	-	3.13E-05	0.19
Acetaldehyde	306	a	8.62E-04	5.3
Acetophenone	25	1.4	3.65E-01	2,261
Acrolein	0.23	0.013	2.09E-05	0.129
Acrylonitrile	38	a	2.79E-05	0.17
Antimony Compounds	13	0.71	1.46E-03	9.0
Arsenic Compounds	2.5	a	4.41E-07	0.0027
Benzene	1,276	a	2.43E-04	1.5
Benzyl Chloride	26	a	3.96E-05	0.25
Beryllium Compounds	0.013	7.07E-04	7.90E-07	0.0049
Biphenyl	38	2.1	1.83E-01	1,130
bis(2-Ethylhexyl) Phthalate	13	0.71	4.80E-04	3.0
Bromoform	7.5	0.42	1.72E-03	11
Cadmium Compounds	0.25	a	1.05E-06	0.0065
Carbon Disulfide	311	18	7.30E-01	4,522
Carbon Tetrachloride	201	a	1.26E-04	0.78
Carbonyl Sulfide	30	1.7	NA	-
Chlorobenzene	1,000	57	1.04E+00	6,442

Chemical	Acute AAC (mg/m^3)	De Minimis (lb/hr)	Chronic AAC (mg/m^3)	De Minimis (lb/yr)
Chloroform	195	a	3.58E-04	2.2
Chromium Compounds	0.10	a	1.58E-07	0.0010
Cobalt Compounds	10	a	6.86E-07	0.0042
Cumene	935	53	4.17E-01	2,583
Cyanide Compounds	3.9	0.22	3.13E-03	19
Dibenzofurans	25	1.4	7.30E-03	45
Dichloromethane (Methylene Chloride)	347	20	4.03E-03	25
Dimethyl formamide	164	9.3	3.13E-02	194
Dimethyl Sulfate	0.31	0.018	NA	-
Ethyl Benzene	250	14	1.04E+00	6,442
Ethyl Chloride (Chloroethane)	1,250	71	1.04E+01	64,420
Ethylene Dibromide (Dibromoethane)	100	a	3.16E-06	0.020
Ethylene Dichloride (1,2-Dichloroethane)	405	a	7.29E-05	0.45
Ethylene glycol	50	2.8	4.17E-01	2,583
Ethylidene Dichloride (1,1-Dichloroethane)	6,250	354	5.21E-01	3,230
Formaldehyde	17	a	1.46E-04	0.90
Glycol Ethers (Surrogate: Diethylene glycol, monobutyl ether)	250	14	3.14E-03	19
Hexachlorobenzene	0.50	a	4.12E-06	0.026
Hexane	11,649	659	2.21E+00	13,689
Hydrochloric Acid	16	0.93	2.09E-02	129
Hydrogen Fluoride (Hydrofluoric Acid)	9.8	0.56	1.46E-02	90
Isophorone	13	0.71	2.09E+00	12,946
Manganese Compounds	2.5	0.14	5.21E-05	0.32
Mercury Compounds	1.0	0.058	3.13E-04	1.9
Methanol	943	53	4.17E+00	25,830
Methyl Bromide	261	15	5.21E-03	32
Methyl Chloride	1,180	67	9.39E-02	582
Methyl Ethyl Ketone	5,015	284	5.21E+00	32,272
MethylHydrazine	0.43	a	3.96E-07	0.0024
Methyl Isobutyl Ketone (Hexone)	500	28	3.13E+00	19,388
Methyl Methacrylate	311	18	7.30E-01	4,522
Methyl Tert-Butyl Ether	1,444	a	7.40E-03	46
N, N-Dimethylaniline	25	1.4	7.30E-03	45

Chemical	Acute AAC (mg/m^3)	De Minimis (lb/hr)	Chronic AAC (mg/m^3)	De Minimis (lb/yr)
Naphthalene	75	a	5.58E-05	0.35
Nickel Compounds	5.0	a	7.90E-06	0.049
Phenol	58	3.3	2.09E-01	1,295
Polychlorinated Biphenyls	2.5	a	1.90E-05	0.12
Polycyclic Organic Matter (Surrogate: Benzo(a)pyrene)	5.0	a	2.02E-06	0.013
Propionaldehyde	403	a	8.62E-04	5.3
Propylene Dichloride	250	14	4.17E-03	26
Selenium Compounds	0.50	0.028	1.83E-02	113
Styrene	554	31	1.04E+00	6,442
Tetrachloroethylene (Perchlorethylene)	814	a	3.20E-04	2.0
Toluene	1,923	109	4.17E-01	2,583
Trichloroethylene	1,450	a	1.68E-05	0.10
Vinyl Acetate	387	22	2.09E-01	1,295
Vinyl Chloride	2,099	a	2.15E-04	1.3
Vinylidene Chloride (1,2-Dichloroethylene)	38	2.1	2.09E-01	1,295
Xylene (Mixed Isomers)	1,736	98	1.04E-01	644

a When the calculated annual de minimis emission rate is lower than the calculated hourly de minimis emission rate, only the annual de minimis rate applies.

4.0 REFERENCES

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